

# CHARACTERIZATION OF DELAYED COKING FEEDSTOCKS AND PRODUCTS BY $^1\text{H}$ AND $^{13}\text{C}$ NMR

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## ABSTRACT

$^1\text{H}$  and  $^{13}\text{C}$  nuclear magnetic resonance spectroscopy has been systematically applied to the characterization of delayed coking feedstocks (petroleum residues) as well as liquid products (naphtha, distillate, oils) and solid products (coke) to evaluate the type and extent of the cracking, polymerization and condensation reactions taking place. NMR results, combined with gas chromatography, elemental analysis and pilot plant data, yield mass balances at the atom-type level. A substantial increase in aromatic type carbons (40 wt%) occurs (for a particular feedstock), primarily at the expense of naphthenic type carbons (35 wt%), and is accompanied by a significant reduction in the number of protons attached to aromatic carbons (80 wt%). This methodology can be used to measure the severity of delayed coking and to estimate product yields and compositions.

## INTRODUCTION

Delayed coking is the most widely used process for the conversion of petroleum residues<sup>(1)</sup>. Residues are pumped through a coker heater, where the temperature is raised to 450-500 °C in a short period of time, and then fed into one of two coke drums (adiabatic reactors). Cracking, polymerization and condensation reactions, initiated in the heater, proceed forming vapors (gases, naphtha, oils) that leave the reactor and are sent to a fractionation tower. A highly viscous carbonaceous material remains in the drum and finally is transformed into a solid product (coke) which can be used (depending upon specifications) as fuel or as filler for the production of carbon anodes (aluminum industry) or arc-electric furnace electrodes (steel industry)<sup>(1,2)</sup>.

Delayed coking feedstocks (vacuum and conversion petroleum residues) contain mainly aromatic hydrocarbons with aliphatic substituents, paraffins, naphthenic compounds and heteroatoms (mostly in heterocyclic compounds). The aromatic components are the network members of the final coke structure; higher aromatic contents give more extended aromatic arrangements and consequently better coke quality due to more ordered domains of oriented molecules<sup>(3)</sup>. On the other hand, reactivity of these feedstocks is related to the number of substituents attached to the aromatic compounds: high aromaticity with only a few substituents (coal tar pitches) corresponds to low reactivity and moderate aromaticity with many substituents (vacuum residues) to high reactivity. A balance is desired for optimum carbonization<sup>(4)</sup>.

Nuclear magnetic resonance ( $^1\text{H}$  and  $^{13}\text{C}$  NMR) is a powerful technique to evaluate delayed coking feedstocks and the corresponding carbonization process, due to its ability to elucidate basic constituents present in these materials.  $^{13}\text{C}$  NMR provides direct measurement of the types of carbon atoms which determine the pyrolysis chemistry<sup>(5)</sup>. Quantitative information is obtained by integrating line intensities. These are proportional to the number of carbon atoms of each type<sup>(6)</sup>. With additional information from  $^1\text{H}$

NMR, average molecular parameters can be derived, and even structural configurations can be drawn (only useful as illustrative tools because these materials embrace a large range of organic molecules as indicated by the broad molecular weight spectra). This constitutes a sound basis for understanding carbonization mechanisms and for comparing different delayed coking feedstocks.

### EXPERIMENTAL

Delayed coking products were obtained in a thermal conversion pilot plant with a 4 lt. reactor capacity operating in continuous up-flow mode at 1500-2000 g/h, 60-140 psig and internal temperature profiles between 400-500 ° C. Gas product was monitored by gas chromatography every 20 minutes and the weighted average reported. Liquid product collected during operation was characterized and later distilled in consecutive ASTM D-86 and D-1160 assays to yield four fractions: naphtha (IBP-400 F), distillate (400-650 F), light oil (650-800 F) and heavy oil (800 F+). Coke was recovered after cooling the reactor.

NMR spectra were collected in a Bruker 300 MSL spectrometer. Liquid  $^{13}\text{C}$  NMR spectra were obtained at 75.468 MHz in a 10 mm probe, using a gated program with decoupler on during acquisition and off during the rest of the experiment to suppress the Nuclear Overhauser Effect. Relaxation times of 5 to 10 seconds were used, 45 pulse angle (corresponding to 5  $\mu\text{s}$  pulse time) and 31  $\mu\text{s}$  for dead time delay. Resolutions of about 1.3 Hz were achieved with receiver gains of 10-30. Liquid  $^1\text{H}$  NMR spectra were obtained at 300 MHz in a 5 mm probe with repeated pulses of 6.1  $\mu\text{s}$ . Band assignments for integrating atomic groups were selected from the extended consensus in the field (reference to TMS standard)<sup>(5,7-8)</sup>:

	$^{13}\text{C}$ NMR		$^1\text{H}$ NMR
Aromatics	110-160 ppm	Aromatics	6.5 -9.0 ppm
-protonated	110-130 ppm	-single ring	6.5 -7.25 ppm
-quaternary	130-160 ppm	-multi. ring	7.25-9.0 ppm
Aliphatics	5- 60 ppm	Aliphatics	0.5 -4.0 ppm
-paraffinics	5- 25 ppm +	-terminal $\text{CH}_3$	0.5 -1.0 ppm
	25- 60 ppm peaks	-internal	1.0 -1.8 ppm
-naphthenic	25- 60 ppm envelope	- $\alpha$ aromatic C	1.8 -3.8 ppm
Olefinic	80-100 ppm	Olefinic	4.5 -6.3 ppm

Gas chromatography data were converted to a similar atom type distribution. Solid state MAS  $^{13}\text{C}/^1\text{H}$  cross-polarization spectra (for cokes)<sup>(9-10)</sup> were obtained at 75.473 MHz and 3500-4000 rpm spinning rates with a proton enhanced pulse program (PENMR).

### RESULTS AND DISCUSSION

Pilot plant data include the distribution of product yields and basic characteristics of feedstocks and products (Table 1).  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra for feedstocks and liquid products are presented in Figures 1-6.

A solid state NMR spectrum for coke is presented in Figure 7. It shows an aromatic carbons peak at the center (100-150 ppm) and two pairs of side-bands. This indicates that only quaternary aromatic carbons and protonated aromatic carbons (that have been calculated to match C/H ratios) are present.

NMR data have been integrated into a weighted distribution (Table 2) and is

compared with the feedstock analysis (Table 3) to determine the differences and to calculate changes (defined by  $\text{Difference} \times 100 / \text{Feedstock}$ ).

It is observed that a significant increase in aromatic carbons (39.4 wt%) occurs, mainly at the expense of a reduction in the naphthenic carbons (-35.0 wt%) with small changes in protonated aromatic carbons (8.5 wt%) and paraffinic carbons (-3.8 wt%). This can be interpreted to mean that the main polymerization/condensation mechanism involves aromatization of naphthenic rings attached to aromatic rings (in this case probably in a 1/1 ratio).

Also, the substantial reduction in protons attached to aromatic carbons (mainly in multiple ring systems) suggests that the carbonization reactions in the liquid phase (leading to coke formation) proceed through benzyl type radicals, while in the vapor phase, cracking reactions substantially reduce the size of the molecules, bringing complex high boiling compounds (present in the feedstock) down to lighter molecules (gas, naphtha, oils).

## CONCLUSIONS

A systematic application of  $^{13}\text{C}$  and  $^1\text{H}$  NMR analysis to delayed coking feedstocks and products results in a quantitative evaluation of the polymerization/condensation reactions and can be used as a measurement of the severity of the process and to estimate product composition.

## BIBLIOGRAPHY

1. Feintuch, H.M. et al., in Handbook of petroleum refining, R.A. Meyer (ed), pp. 3-61 (1986).
2. De Biase, R. et al., in Petroleum Derived Carbons, ACS, pp. 155-171 (1986).
3. Winter, L.L., Kirk-Othmer Enc. Chem. Tech., pp.570-576 (1978).
4. Mochida, I. et al., Oil Gas J. 86(18):73-77 (1988).
5. Seshadri, K.S. et al, Fuel, 61(4):336-340 (1982).
6. Gillet, S. et al., Fuel, 60(3):221-225 (1981).
7. Cookson, D.J. and Smith, B.E., in Coal Science and Chemistry, A. Volborth (ed), pp. 31-60 (1987).
8. Yamashita, G.T. et al., Preprints ACS Div. Petroleum Chem., 34, (2) 301-305 (1989).
9. Nakamizo, M. and Adacchi, Y., 19th Bienn. Conf. Carbon, pp. 148-149 (1989).
10. Hinckley, C.C. et al., SIU Carbondale, Sixth Ann. Conf. Mater. Techn. Center, pp. 14-31 (1990).

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Table 1. Delayed coking pilot plant data

Material	Yield wt%	Boiling range, °F	API gravity	Impurities wt%
Feedstock	-	350-600	14.6	3.03
Gases	10.31	-	-	0.22
Naphtha	24.66	IBP-400	57.9	0.25
Disillate	26.57	400-650	30.2	1.88
Light Oil	12.33	650-800	15.3	3.24
Heavy Oil	7.84	800+	4.6	3.88
Coke	18.28	-	-	4.47

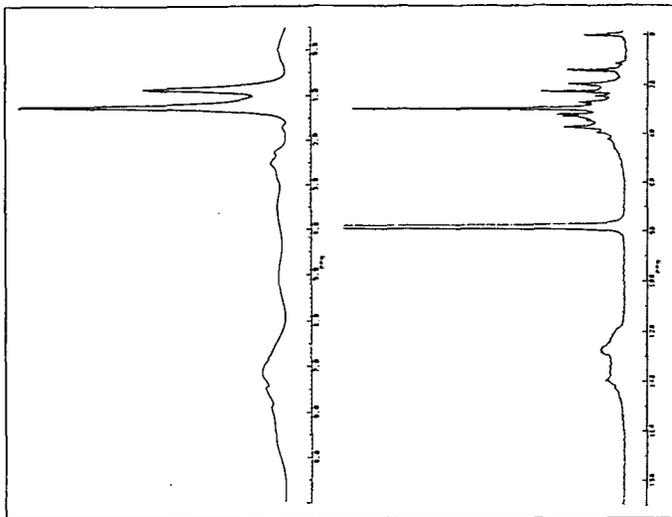


Figure 1.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of a delayed coking feedstock

Table 2. Distribution of proton and carbon atoms in delayed coking products

Atom type wt%	Gas wt%	Naphtha wt%	Distillate wt%	Light Oil wt%	Heavy Oil wt%	Coke
CARBON	8.12	21.54	23.01	10.67	6.80	17.28
Aromatic	0.00	4.27	6.14	4.18	3.26	17.28
-protonated	0.00	2.13	2.95	2.10	1.73	2.16
-quaternary	0.00	2.14	3.20	2.07	1.53	15.12
Aliphatic	7.64	17.28	16.87	6.50	3.55	0.00
-paraffinic	7.64	13.83	10.14	4.03	2.36	0.00
-naphthenic	0.00	3.45	6.72	2.47	1.19	0.00
Olefinic	0.48	0.00	0.00	0.00	0.00	0.00
PROTON	1.98	3.06	3.06	1.26	0.74	0.18
Aromatic	0.00	0.12	0.17	0.19	0.13	0.18
-single	0.00	0.07	0.11	0.06	0.03	0.00
-multiple	0.00	0.05	0.07	0.13	0.10	0.18
Aliphatic	1.88	2.83	2.83	1.04	0.59	0.00
-terminal	1.58	1.15	0.84	0.24	0.12	0.00
-internal	0.31	1.47	1.57	0.58	0.34	0.00
- $\alpha$ arom. C	0.00	0.20	0.41	0.22	0.13	0.00
Olefinic	0.06	0.11	0.06	0.03	0.01	0.00

Table 3. Atom type balances in delayed coking reactions

Atom type	Feed wt%	Products wt%	Difference wt%	Change %
CARBON	85.99	87.43	+ 1.44	+ 1.68
Aromatic	25.19	35.13	+ 9.93	+39.42
-protonated	10.20	11.07	+ 0.87	+ 8.53
-quaternary	15.00	24.06	+ 9.06	+60.40
Aliphatic	60.79	51.82	- 8.97	-14.76
-paraffinic	39.50	37.99	- 1.51	- 3.82
-naphthenic	21.29	13.83	- 7.46	-35.04
Olefinic	0.00	0.48	+ 0.48	+
PROTON	10.98	10.26	- 0.72	- 6.56
Aromatic	3.89	0.80	- 3.09	-79.52
-single	1.11	0.27	- 0.84	-75.85
-multiple	2.78	0.53	- 2.25	-80.98
Aliphatic	7.09	9.17	+ 2.07	+29.21
-terminal	2.14	3.93	+ 1.79	+83.52
-internal	4.37	4.27	- 0.10	- 2.22
- $\alpha$ arom. C	0.58	0.96	+ 0.38	+65.37
Olefinic	0.00	0.27	+ 0.27	+
H2	-	0.03	+ 0.03	+

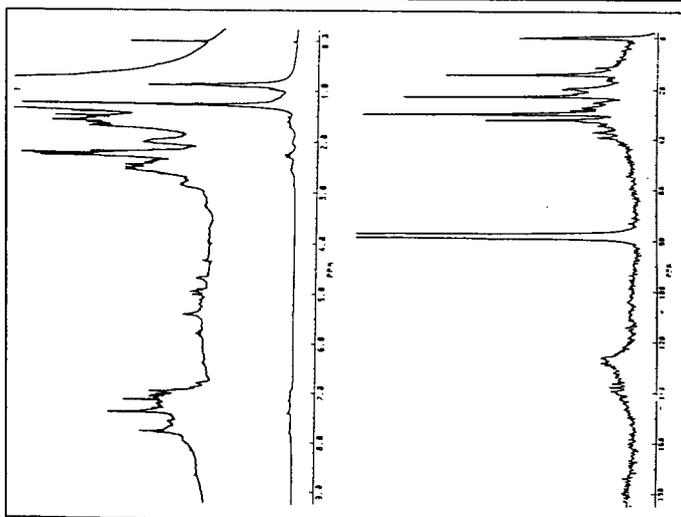


Figure 2.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of a delayed coking liquid product

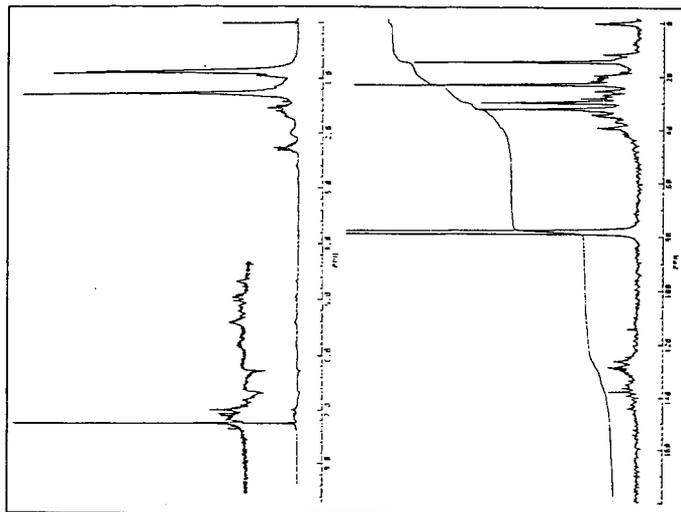


Figure 3.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of a delayed coking naphtha

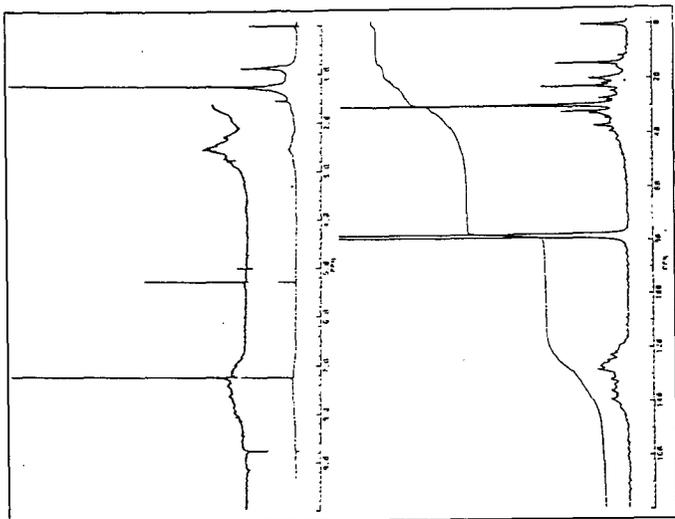


Figure 5.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of a delayed coking light oil

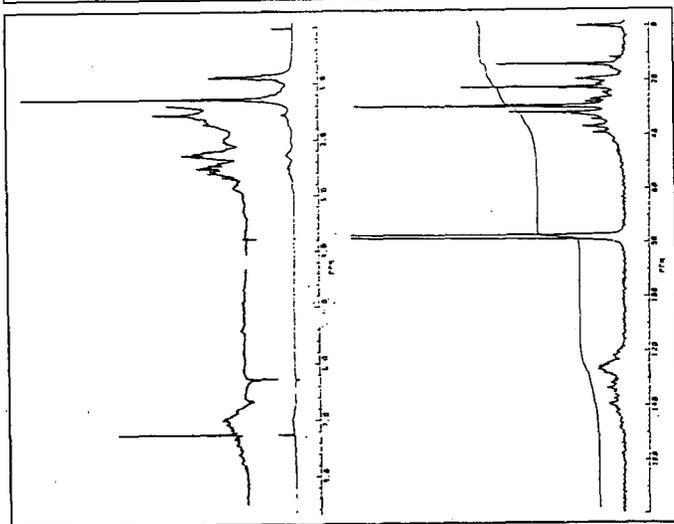


Figure 4.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of a delayed coking distillate

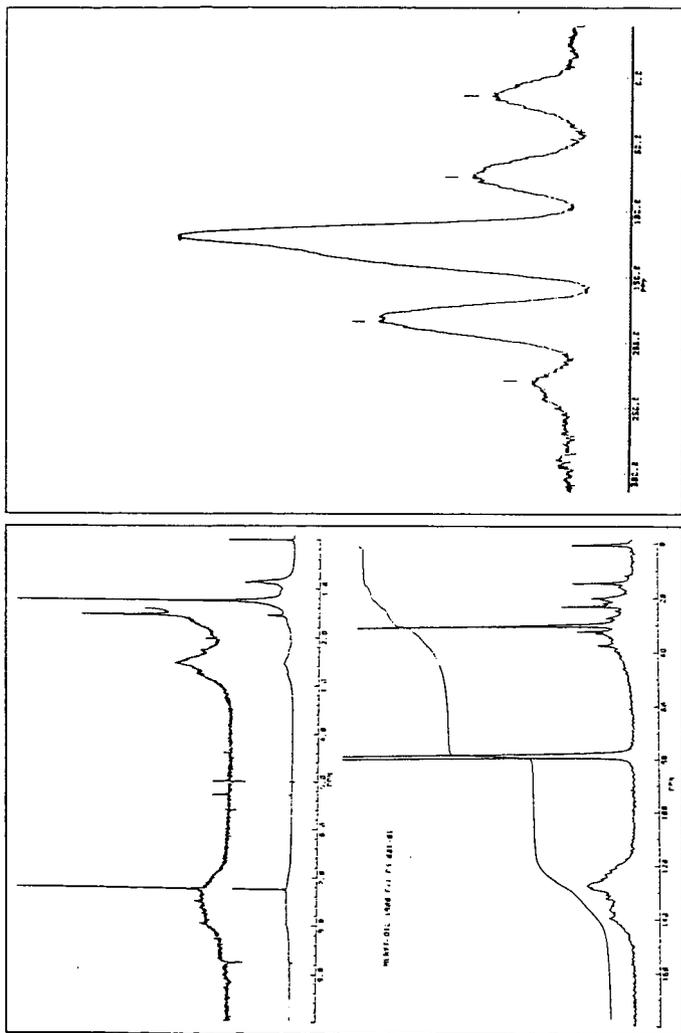


Figure 6.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of a delayed coking heavy oil

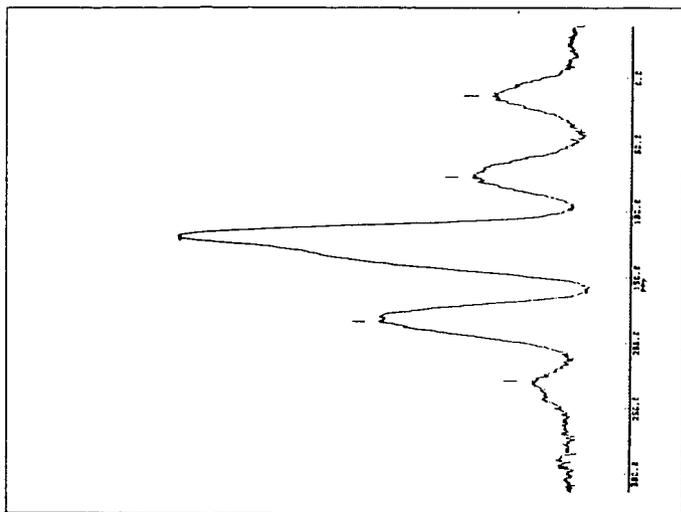


Figure 7.  $^{13}\text{C}/^1\text{H}$  crosspolarized MAS NMR spectrum of a petroleum coke